

Effect of crossing geometry on the plasmonic behavior of dielectric core/metal sheath nanowires

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We have shown that dielectric/metal composite nanowires exhibit very strong surface enhanced Raman spectroscopy (SERS) signals when arranged in a random three-dimensional geometry. Since the intersections of the nanowires are critical in generating the high electric fields necessary for this enhancement, we are investigating this effect under more controlled conditions. We examined nanowire arrays formed by e-beam lithography and we have examined the plasmonic effects, both longitudinal and transverse, due to changes in crossing geometry by specific placements of dielectric/metal nanowires on these arrays. Results indicate significant angular effects on the SERS enhancement supported by electric field calculations. © 2009 American Institute of Physics. [DOI: 10.1063/1.3094129]

Optically based sensing provides advantages over electronic sensing because optical spectra can uniquely fingerprint a chemical compound, eliminating false alarms and simplifying the detection process. In Raman scattering (RS), light is scattered from a chemical of interest, and the vibrational modes in the chemical redshift the frequency of the scattered light, producing a spectrum of lines that are characteristic of that molecule.

Although ordinary RS results in low sensitivity (10^{-8} of the exciting laser), the Raman signal can be enhanced by many orders of magnitude by the use of metal nanoparticles¹ and metal shell/dielectric core nanoparticle composites.² This enhancement is thought to be the result of local electromagnetic fields that are created by the laser excitation of localized surface plasmons at the metal surface. Even though enhancements as high as 10^8 – 10^{12} have been reported for different nanostructures,³ the underlying mechanisms are not yet fully understood. This is evidenced by theoretical calculations which predict surface enhanced Raman spectroscopy (SERS) enhancements that are many orders of magnitude greater than have been experimentally attained.²

Thus, understanding the SERS mechanism and how it relates to the geometric properties (effects of transverse and longitudinal modes) of a SERS substrate is critical to any possible future applications in highly efficient sensors and taggants. This information is also required for the reproducibility of the enhanced signal and the reliability of SERS surfaces. Current research with metallic nanoparticles suggests that the size, shape, and chemical effects are important parameters in the SERS effect.^{4–6} For example, it has been shown that Au nanorods exhibit a stronger SERS effect than Au nanoparticles,⁷ and the plasmon resonance and the strength of the electric field can be tuned in metal/dielectric nanodisks.⁸ In addition, special alignment also resulted in higher SERS intensity,⁹ as well as close proximity of the nanostructures to each other, which produce electric field hot spots that are caused by coupled plasmon modes.^{2,10}

We have developed a highly sensitive SERS material based on a random distribution of dielectric core/metal shell

nanowire geometry,^{11,12} which can reliably detect 0.2 pgm of rhodamine 6G (Rh6G) (a standard SERS-active dye). The SERS enhancement for these experiments was greater than 10^8 , with the fluorescence being three to five orders of magnitude greater.¹² We believe that the random distribution of dielectric core/Ag nanowires is important because it maximizes the density of hot spots (high electric field regions) and allows molecules more access in depth than nanoshell geometries. However, the role of geometric effects in relation to the angular dependence of the SERS enhancement of crossed wires have not been shown.

In order to elucidate the role of transverse and longitudinal plasmon coupling and the correlation to nanowire crossing geometries, we have investigated SERS enhancements for several e-beam lithographically produced Au nanowire lines combined with various crossing angles of superimposed dielectric core/Ag sheath nanowires. We then compare the resultant SERS with COMSOL (Ref. 13) finite element electric field calculations as a function of geometries. Our results indicate very good agreement between experiment and theory and provide insight into why random distributions of crossed wires may form a very efficient and uniform SERS substrate.

The growth of the Ga₂O₃ nanowires was achieved by the controlled oxidation of pure Ga metal in a vacuum tube furnace.¹⁴ The source material was placed at one end of a 4 in. alumina boat, with the substrate placed at the other end. The boat was then inserted into a quartz tube inside a tube furnace, which was evacuated to a base vacuum of 40 mTorr using a mechanical pump. The furnace was then heated to 900 °C and growth was initiated using a 6:1 flow ratio of Ar to O₂. The Au lines, of 80 and 95 nm widths, with 186 nm wire to wire spacing, were produced by e-beam lithography. Two types of Au lines were fabricated, those that were 20 nm high and those that were 65 nm high. All the grown nanowires were analyzed using a LEO SUPRA 55 scanning electron microscope (SEM), JEOL 2010F 200 KV high resolution transmission electron microscope (HRTEM) and x-ray energy dispersive spectroscopy attached to the HRTEM, as well as Raman spectroscopy.

The SERS measurements were performed using a custom μ -Raman system that is composed of a Mitutoyo micro-

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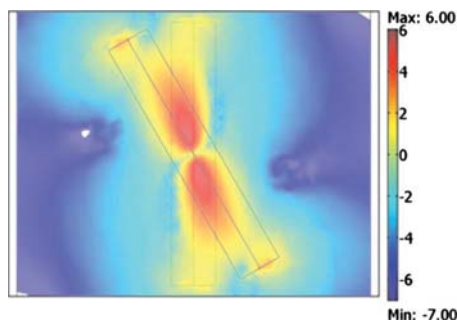


FIG. 1. (Color online) COMSOL electric field calculation of Ag nanowires crossed at 30° in response to 500 nm wavelength light polarized in the x direction.

scope, an Ar ion laser, and an Ocean Optics QE65000 fiber based spectrograph with 10 cm^{-1} spectral resolution. The Ar laser had wavelengths of 457, 488, and 515 nm. The Raman excitation were performed through the microscope with a 100 times objective with numerical aperture=0.9. The laser spot had a diameter of $0.75\text{ }\mu\text{m}$. The microscope was equipped with an Olympus $10\times$ digital camera for imaging the sample and for aligning the laser spot. The Raman measurements were performed with a laser polarization that was parallel to the lithographic lines.

The SERS enhancement was simulated by solving Maxwell's equations in the quasistatic approximation, which is appropriate for geometries smaller than the wavelength of light. In this case, the diameters of the Ag coated nanowires were 60 nm and had lengths of 300 nm. The Au lithographic patterns were approximated by boxes that were 400 nm in length, 90 nm wide and 90 nm high. The quasistatic approximation has been shown to be valid for these dimensions by comparing to a full solution of Maxwell's equations.¹⁵

We have previously shown that $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowire composites can be very efficient SERS substrates,^{11,12} and we suggested that the nanowire crossings result in "hot" spots¹² in the electric fields, thus enhancing the SERS signal. The importance of plasmon coupling at nanowire crossings can be seen in Fig. 1, which is a result of a finite element simulation¹² of the electric field near two obliquely crossed nanowires in air. An enhanced plasmon resonance is found in the vicinity of the crossing, with the maximum away from the crossing angle, in a much expanded volume surrounding each crossing. This would not only enhance the SERS effect due to the strong coupling, but allow more molecules to enter this high electric field region, thereby enhancing the SERS sensitivity. Furthermore, the parallel wire geometry,¹⁶ as well as the nanosphere geometries, require a very specific spacing in order to maximize the enhancement due to coupling. This is not the case in crossed wires, since an optimal spacing will always be present for every crossing angle due to the wire geometry.

Since we cannot control the geometry in a random nanowire ensemble, it is difficult to examine the effects of crossing angle in more detail. However, a more ordered wire structure does allow the study of the effects of crossing geometry, and we have produced such structures by e-beam lithography. These ordered structures consisted of 80 or 95 nm Au lines, spaced 186 nm apart, with heights of 60 nm. Although a very weak SERS signal was noted for Rh6G, no SERS was obtained for benzene thiol (BZT). This is not surprising, since the Au lines were spaced 186 nm apart,

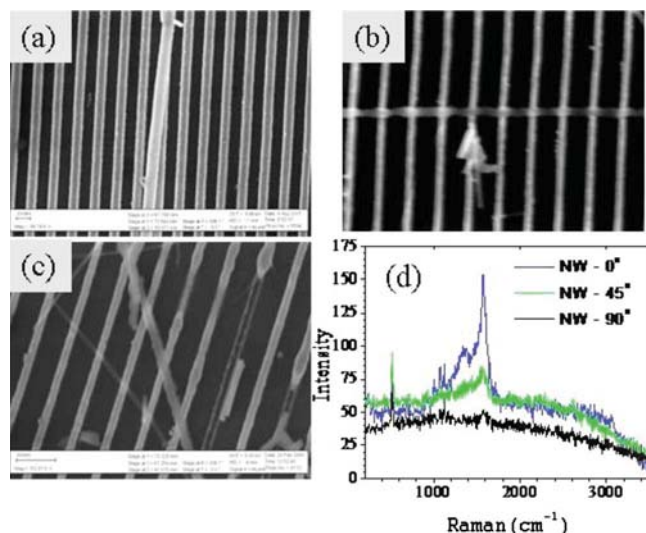


FIG. 2. (Color online) (a) Parallel, (b) perpendicular and (c) angled $\text{Ga}_2\text{O}_3/\text{Ag}$ NW along Au grating and (d) resultant SERS for BZT.

where one would not expect effective plasmon coupling between the wires.

In order to examine the effect of crossing geometry in more detail, we used these Au lithographically produced lines, combined with the placement of individual $\text{Ga}_2\text{O}_3/\text{Ag}$ nanowires in specific crossing angles. In this case, in order to reduce the fluorescence, we have chosen to use BZT, which does not experience excitation using the 514.5 nm laser line. A number of nanowire crossing geometries were obtained, including parallel, perpendicular, and angled, as shown in Fig. 2. It should be noted that the spacing between the dielectric core/metal nanowires and the underlying Au lines was the same for all measurements. Only the crossing angle was changed, which allows us to examine the effects of the transverse and longitudinal components of the SERS. Figure 2(d) shows the SERS signal obtained from the application of BZT to the various nanowire crossing geometries shown in Figs. 2(a)–2(c). It is clearly seen that the parallel geometry [Fig. 2(a)] exhibits the highest SERS signal, while the perpendicular geometry [Fig. 2(b)] is the weakest. SERS for the 45° angled crossing is intermediate in signal strength.

In order to understand this result, let us briefly consider the expected electric field enhancement for wires as a function of angle between each other obtained from the COMSOL simulation, shown in Fig. 3. As can be seen from the simulation, one would expect a much larger enhancement from

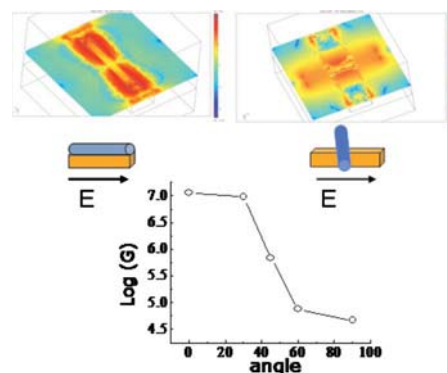


FIG. 3. (Color online) COMSOL calculation of the expected SERS enhancements for parallel and perpendicular wire orientation.

nanowires which are nearly parallel, similar to the SEM image of the parallel wires in Fig. 2(a). The perpendicular wire should exhibit much lower SERS enhancement in this geometry, which is confirmed by the data in Fig. 2(d). The nanowires crossed at 45° exhibit a SERS strength between the two extremes, which is confirmed by the electric field calculations in Fig. 3 of the SERS enhancement $G=(E_{\text{tot}}/E_{\text{inc}})$.⁴

These results have significant implications in relation to the previously observed work on SERS from random arrays of crossed nanowires. It was observed that the random configuration produced very good uniformity. This is a direct result of the fact that due to the randomness, one would expect 50% of the wires would always have a component of the laser polarization parallel to the long axis of the wire. Since the total measured response from a collection of randomly distributed and randomly crossed nanowires is the sum over all nanowires and all geometries, rotations of the sample would have little effect on the SERS response of such a sample. Furthermore, the polarization of the exciting laser will also have a minimal effect. The tradeoff for this uniformity is the highest possible SERS enhancement.

In summary, we have examined the effect of crossing geometry on the electric field enhancement in the SERS effect, using dielectric/metal nanowire composites and Au lines produced by e-beam lithography. These results indicate that specific geometries leading to electric field hot spots can significantly enhance the SERS signal from target molecules, with closely spaced parallel nanowires showing the largest effect. The 45° crossed wires still exhibited strong SERS, and they have the further advantage of large effective E field regions, which allow more molecules access, resulting in

more uniform and repeatable SERS measurements. Finite element calculations support the angular dependence of the SERS enhancement results obtained experimentally.

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